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On the generalized zeroth law of thermodynamics

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Abstract : A generalized zeroth law of thermodynamics has been formulated which takes in its fold all nonequilibrium and equilibrium states of a thermodynamic system. The need for the use of the most efficient temperature measuring techniques, particularly in the case of nonequilibrium, has been restressed. It is shown that the quality of temperature remains the same in going from equilibrium to nonequilibrium which conforms well also with the kinetic theory meaning of it.

Keywords : Zeroth law of thermodynamics, temperature, nonequilibrium thermodynamics.

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1. Introduction

The concept of temperature for nonequilibrium states, troubles scientists considerably. The contemporary position in resolving the problem is that of nonunanimity amongst the thermodynamicists. For example, in the literature, one finds the usage of the terms nonequilibrium temperature and the contact temperature. The latter one is defined [1,2] through the temperature of that heat reservoir which when brought in diathermal contact with a nonequilibrium system produces no heat flux across their boundaries in contact. However, this temperature concept brings in the corresponding irreversible thermodynamic description the thermodynamic parameters of the said hypothetical heat reservoirs [2]. In real processes, each interior position of a thermodynamic system evolves under the constraints offered by its immediate neighbours besides its own internal ones. Hence, the variation of heat flux at a given position in a system is determined, if not completely, by the condition of the temperature gradient imposed upon by its neighbourhood. Therefore, the temperature involved in controlling the real processes needs to be one belonging to the system in nonequilibrium.

On the other hand, the term nonequilibrium temperature primarily originates in the formalism called extended irreversible thermodynamics [3,4] and is stressed to be a distinctly different physical entity than the temperature in the case of equilibrium. This led to an unfortunate debate about the meaning of temperature in nonequilibrium [5]. But if a local equilibrium is believed to exist in a system then even in the presence of a heat flux, the temperature is considered as well defined and taken as the same physical entity as that is given by the zeroth law of thermodynamics in equilibrium [3,6]. Recently, particularly with reference to the extended irreversible thermodynamic framework, it has been demonstrated [7] that the temperature concept retains the same physical meaning whether the system is in equilibrium or not. Thus, it is the absolute temperature on the Kelvin scale, and no other, which appears in thermodynamic description of a system whether in nonequilibrium or in equilibrium. We have come to the same conclusion [8] by comparing the act of temperature measurements in the cases of equilibrium and nonequilibrium.

Whenever, one speaks of a difficulty in rigorously defining temperature in nonequilibrium, it is with respect to the systems having spatial nonuniformities such as in pressure, velocity, temperature, concentration *etc.* The case of a chemical reaction occurring at a finite rate in a spatially uniform system, is indeed a case of nonequilibrium and at times, it happens to be considerably far away from equilibrium, however, in general, no doubt has been spelled out about the quality of the temperature function used in its thermodynamic (irreversible) description. Hence, one believes that the thermostatic definition of temperature

based on the zeroth law of thermodynamics, applies to the chemically reacting systems [6]. This then leads us to believe, in practice, that some nonequilibrium situations are of different type than the others. From thermodynamic point of view, in our opinion, it is not in a proper spirit.

On a close scrutiny, we find that all the above mentioned incoherencies crop-up because no attempts have been made so far to augment the zeroth law of thermodynamics to include the nonequilibrium states in its fold. Muschik's efforts [1,2] are the only ones in which a direct use is made of the zeroth law of thermodynamics. That is, he uses the equilibrium statement (the conventional one) of the zeroth law of thermodynamics by using the heat reservoirs and the result is the emergence of the entity called the contact temperature. However, as demonstrated below, all the difficulties get overcomed by the suitable augmentation of the zeroth law of thermodynamics. In next section, we describe the relevant aspects of temperature concept which in turn, paves the way for the required augmentation of the zeroth law of thermodynamics and the latter one we describe in Section 3. The final section comprises of the concluding remarks. By this augmentation of the zeroth law of thermodynamics, we firmly establish that whether the system is in equilibrium or not, the quality of temperature remains identically the same and any irreversible thermodynamic description obviously involves it.

2. Some of the relevant facts about temperature

2.1. Phenomenological level of considerations :

The zeroth law of thermodynamics identifies a thermodynamic function named temperature which is equal for two systems when they are in thermal equilibrium with each other [9]. The temperature is measured by a device called thermometer in that the tiny bulb of it is thermally equilibrated with a local position within the system whether it is in equilibrium or not. Therefore we consider one of the simple versions of the fluid dynamical internal energy balance equation [10], namely :

$$\rho \frac{du}{dt} = -div\boldsymbol{q} - p\rho \frac{dv}{dt} + \mathbf{II} : \nabla \boldsymbol{u} \qquad (1)$$

where ρ is the mass density, u is the per unit mass internal energy, $\boldsymbol{q}$ is the so called heat flux density, p is the pressure, $v(= \rho^{-1})$ is the specific volume, $\mathbf{II}$ is the dissipative stress tensor, $\boldsymbol{u}$ is the barycentric velocity and t is time.

Further recall that when a stable temperature reading in thermometer is attained the internal energy of the thermometric fluid remains constant in time when the system is in equilibrium. Since no mechanical interactions of the thermometer with the system in question are involved eq. (1) requires that,

$$\frac{du}{dt} = 0 \text{ that is } u = const.\} : \rightarrow div\boldsymbol{q} = 0 \qquad (2)$$

But since no heat flux exists in a system when it is in equilibrium therefore when the temperature is recorded at that moment no heat flux can exist within the tiny volume element of the thermometer. Hence, at the time of the stable temperature reading not only the divergence of the heat flux vanishes but also the heat flux itself becomes zero in the tiny volume element of the thermometer. Whereas when there exists a heat flux in the system the thermal equilibration of the local position of the nonequilibrium system and the temperature measuring device only requires the divergence of the heat flux to vanish within the tiny volume element of the thermometer in contact and not the heat flux itself. This is the mechanism by which the momentary stable temperature reading gets recorded [8].

2.2. Microscopic level of considerations :

Indeed when our discussion of a thermodynamic system is at the phenomenological level one should not bring in the microscopic considerations But in order to have a clear understanding it is profitable to consider the following Recall that a temperature measuring device interacts with a system as a tiny closed system. Hence, the heat flux which gets temporarily generated within the tiny volume element of the thermometer contains no contribution from the matter diffusion even if it is occurring in the system. That is the communication of energy between the thermometer and the system is by the conduction mechanism only. From the considerations of the microscopic level of events one finds that in the conduction mode of energy communication the chaotic translational and the internal degrees of freedom of the molecules can participate. However, the internal degrees of freedom of the molecules are by several orders less efficient in energy communication than the chaotic translational mode [11]. Of course, in the case of a system in equilibrium one can afford to wait for a longer time duration. By this the internal degrees of freedom of the molecules also get a chance to participate in the energy communication mechanism. However the temperature recorded by a highly efficient temperature measuring device (such as the one used in the nanosecond T-jump method [12] and likes) or that by a conventional thermometer will give an identically same value of temperature because in equilibrium there exists an equipartition of energy in the various degrees of freedom of the molecules [13]. Thus out of the above two methods of the temperature measurement in the former case only the chaotic translational motion of the molecules is able to communicate energy whereas that in the latter case all degrees of freedom of the molecules participate in the energy communication. From this discussion it is clear that the temperature of the system is basically determined by the average of the energy contained in the chaotic translational motion of the molecules.

In support of this deduction consider how T-jump is achieved in the nanosecond T-jump method [12]. An iodine laser is used to pump energy into the vibrational-rotational energy levels of the water molecules (near-IR relaxation time $\tau \sim 10^{-13}$ s [14]). The dissipation of the excess energy from the vibrational-relaxational excited state causes the temperature of the system to rise by about one Kelvin unit that too in a few nanoseconds. This example clearly demonstrates that the temperature of the system is basically determined by the average of the translational energy of the chaotic motion of the molecules. Indeed, this is the very meaning which remains in the back of one's mind when he uses the term thermal energy. Moreover, this is exactly how one identifies temperature in the kinetic theory [5]. For example, in the case of a perfect gas whose molecules have internal degrees of freedom the kinetic theory expression is,

$$nk_BT + nu_{\text{int}} = \sum \int m\left(\frac{1}{2}C^2 + \epsilon_i\right) f_{ci}\, dC \qquad (3)$$

where n is the number density of molecules, k_B is the Boltzmann constant, T is the temperature, u_{int} is the average energy per molecule in the eigen states of the internal degrees of freedom of the molecules, m is the mass of a molecule, $C(=v-u)$ is the chaotic velocity of the molecules, v is the molecular velocity, u is the barycentric velocity, ϵ_i is the energy of the i-th eigen state of the internal degrees of freedom of the molecule and f_{ci} is the distribution function. Thus if one uses the equilibrium distribution function the result of the integration in eq. (3) corresponds to an equilibrium state and if f_{ci} is that for a nonequilibrium state, such as when a nonuniformity exists, the result of the intergation would be that for a nonequilibrium state. Notice that eq. (3) clearly tells us that the temperature of the system in kinetic theory is basically determined by the energy contained in the chaotic translational motion of the molecules irrespective of the state of the system being that of equilibrium or nonequilibrium.

2.3. Deductive assertions and certain practical suggestions :

Thus as said above the energy communicated by the thermal interaction between a tiny volume element of thermometer and an interior position of a system (and for that matter even between the bouding surface of a closed system and the thermometer) is that due to the conduction mode only. In order to ratain the identically same quality of the measured temperature both in equilibrium and in nonequilibrium situations of a system one is supposed to use the highest efficient temperature measuring device. By this he remains absolutely sure that the experimentally recorded temperature is due to the energy exchanged by the thermometer only with the chaotic translational motion of the molecules of the system. For the same reasons it is not difficult to realize that the irreversible processes of the system sense and respond to this very temperature. Since at any given position in the system in nonequilibrium the temperature, along with a host of other properties, can be a time dependent quantity, therefore, it is required to know that how fast a reliable temperature reading can be recorded. In other words, one needs to know what is the minimum time required for the attainment of the condition of eq. (2) within the tiny volume element of a thermometer. An answer to this question is that the relaxation time for the vanishing of the divergence (not in an isolated state) of the heat flux hardly goes beyond a picosecond in condensed phases [3]. This then clearly puts a limit on the irreversible processes which come under the purview of thermodynamics. That is any process faster than the time required to register the temperature by a most efficient device remains beyond the scope of thermodynamics. Of course, in stressing this we are contemplating that the experimentally measured temperature coincides with the thermodynamic one provided by the generalized zeroth law of thermodynamics described in the next section.

3. The generalized zeroth law of thermodynamics

Before formulating the generalized zeroth law of thermodynamics covering nonequilibrium states let us recall that a point mass of a fluid considered in the continuum dynamics [16], in fact, is a tiny volume element from the microscopic point of view which contains a very large number of molecules so that it can be treated as a tiny thermodynamic system [17,18]. The state of these molecules (the collective one) determines whether there exist the flux densities of various quantities or not. The constraints under which each point mass evolves is also determined by the neighbouring point masses which give rise to the existence of gradients of various quantities. Hence when a point mass is instantly isolated then all the gradients also vanish instantly but the fluxes remain as they were just before the act of the isolation and then they die out with the passage of time. Keeping the above in mind and also Muschik's generalization of the observations on the thermal interactions in nonequilibrium we generalize the zeroth law of thermodynamics and bring the nonequilibrium states too in its fold, which reads as,

> "When three tiny volume elements are simultaneously and instantly isolated from the respective nonequilibrium systems and in the same instant action they are brought into diathermal contacts as closed systems 1 with 2 and 2 with 3. If within the short time limit of the sensing of the thermal interactions it is found that 1 is in momentary thermal equilibrium with 2 and 2 is with 3 then 3 is also in the momentary thermal equilibrium with 1. The momentary thermal equilibrium means that if the volume elements had the heat fluxes then they remain unaffected during the minimum short period of thermal interactions and if no

heat flux existed, both such nonequilibrium and the equilibrium states included, no heat flux gets generated during the said diathermal contact. The making of a diathermal contact between the tiny volume elements one of which having a heat flux and the other without it is not forbidden".

The above statement at once assigns a common state function to the tiny volume elements during their momentary thermal equilibration, which is easily identified as thermodynamic temperature. Once the generalized zeroth law of thermodynamics guarantees the existence of a temperature function for nonequilibrium states of a system one is then free to coincide it with the absolute temperature on the Kelvin scale. Moreover, the short period envisaged in the attainment of the momentary thermal equilibrium matches well with the time required to register the temperature by a most efficient device. The choice to coincide also the thermodynamic temperature in nonequilibrium with the absolute temperature on the Kelvin scale imparts a thermodynamic status also to experimentally measured temperature in the case of nonequilibrium. Also notice that the above statement of the generalized zeroth law of thermodynamic has the following features, namely :

(1) although in the preceding section we have discussed the relevant microscopic aspects but the above statement consists only of the macroscopic ones.

(2) it maintains the identically same quality of thermodynamic temperature in going from equilibrium to nonequilibrium.

(3) for the identification of a temperature function for nonequilibrium states at no stage it requires a help of heat reservoirs in Muschik's sense and hence it does not lead to the concept of the contact temperature.

(4) the temperature function provided by it belongs to the system whether it is in equilibrium or in nonequilibrium, that is it is an existing property of the system unlike the contact temperature.

(5) it includes all nonequilibrium situations.

Finally, it is necessary to stress (which sometimes gets overlooked) that the direction of the heat flow is a matter of our experience which forms the basis of the second law of thermodynamics. Therefore, it is not a business of the zeroth law of thermodynamics and hence that of the generalized zeroth law of thermodynamics to predict it. Actually, both the versions of the zeroth law are incapable of doing this job.

4. Concluding remarks

A long pending demand of the legalization of the concept of temperature in noneequilibrium has been accomplished by the generalized zeroth law of thermodynamics stated in the preceding section. For this very purpose several battles have been fought in the past some of them have been cited herein [1–8]. The statement of the generalized zeroth law of thermodynamics paves the way to systematically tackle the development of an irreversible thermodynamic description based on the laws of thermodynamics, this job still remains unaccomplished or partly accomplished in the literature [18,19]. We are investigating it further and would shortly describe our results in a separate paper. Since all nonequilibrium situations are equally covered by the generalized zeroth law of thermodynamics it is, therefore, expected that in developing an irreversible thermodynamic description no priori knowledge should be a must of the applicability or nonapplicability of the famous local equilibrium hypothesis [6,7].

Earlier, we have propounded an universal inaccessibility principle (UIP) [20] and showed that it is a local level analogue [21] of the second law of thermodynamics. That is as the Carathéodory principle [9] provides an entropy function in equilibrium similarly the UIP provides an entropy function in nonequilibrium. Therefore, as in the case of equilibrium there exists a correspondence in reference to the thermodynamic temperature function for equilibrium between the equilibrium part of the second law of thermodynamics or the Carathéodory principle and the zeroth law of thermodynamics a similar correspondence now holds between the generalized zeroth law of thrmodynamics and the UIP with reference to the thermodynamic temperature in nonequilibrium.

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